PATENT SPECIFICATION

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C3R 36C10 36C12 36C13P 36C19 36C22 36C24 36C28X 36C33B 36C5B1 36C6AX 36C6X 36C8P 36C8R 36D1 36D2 36L1B 36L4C 36L5X 36L6D 36L6F 7C10 7C12 7C13P 7C19 7C22 7C24 7C28X 7C33B 7C5B1 7C6AX 7C6X 7C8P 7C8R 7L1B 7L4C 7L5X 7L6D 7L6F 7S

(19)

(72) Inventors VICTOR JEFFREY LESLIE and RAYMOND BARRY VICCARS

(54) AROMATIC POLYMERS

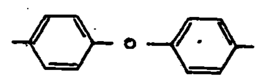
(71) We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, Imperial Chemical House, Millbank, London SW1P 3JF, a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

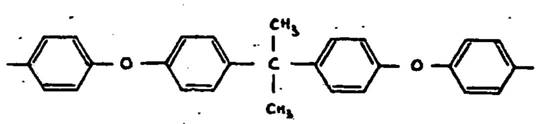
This invention relates to thermoplastic polymer compositions and in particular to aromatic polysulphones having improved thermal stability.

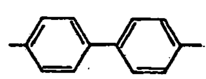
According to the present invention, a thermoplastic polymer composition is provided having improved thermal stability comprising at least one aromatic polysulphone consisting of repeating units having the structure

$$—Ar—SO_2—$$

wherein Ar, which may vary from unit to unit in the polymer chain, is a bivalent aromatic radical selected from







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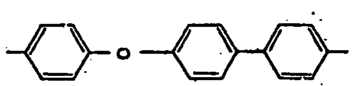
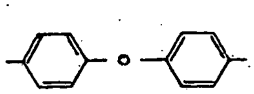
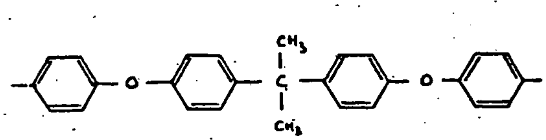
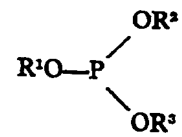


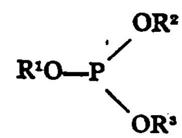
at least some of said Ar radicals being

 and/or 

and at least one phosphite ester, the amount of said phosphite ester being 0.01 to 4% by weight, based on the combined weights of the phosphite ester and polysulphone, said phosphite having the formula



in which R^1, R^2 and R^3 are selected from hydrogen and univalent hydrocarbon or halohydrocarbon radicals, as hereinbefore defined, provided that not more than one of R^1, R^2 and R^3 is hydrogen, or R^1, R^2 and/or R^3 taken together form a multivalent hydrocarbon or halohydrocarbon radical, as hereinafter defined, linking a) two or more phosphite groups of the formula

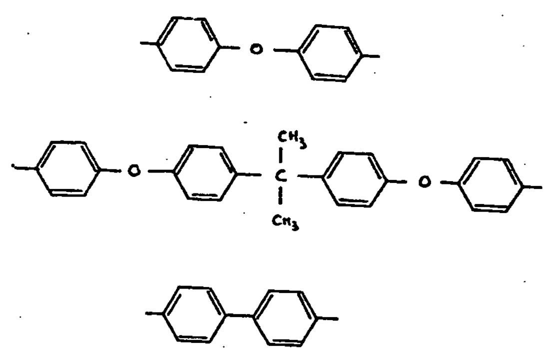


or b) at least two oxygen atoms of the same phosphite group.

The aromatic polysulphones that are used in the present invention comprise repeating units of the formula

$$—Ar—SO_2—$$

in which Ar is a bivalent aromatic radical, which may vary from unit to unit in the polymer chain (so as to form copolymers of various kinds), selected from



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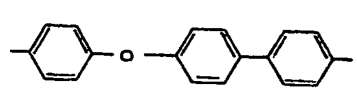
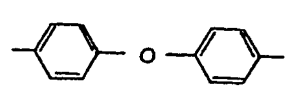


at least some of the Ar radicals being



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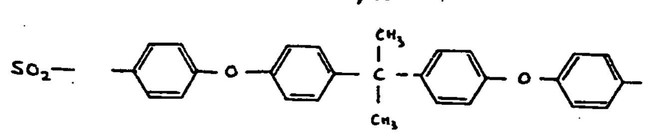
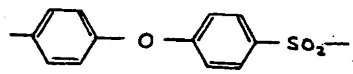


One commercially available polysulphone has the repeating units of the formula



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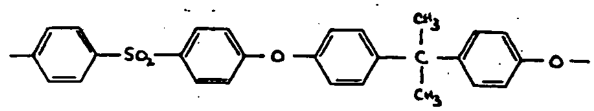
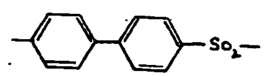
(Imperial Chemical Industries Limited). Another commercially available polysulphone is said to have repeating units of the formula



II

(Union Carbide Corporation), while another is said to have copolymerised units in various proportions of the formulae



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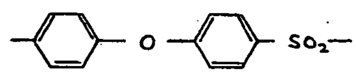
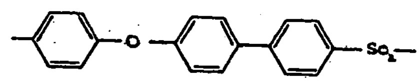
and



I

(Minnesota Mining and Manufacturing Company). Another group of aromatic polymers has repeating units of the formula



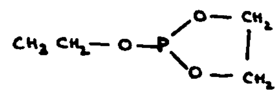
IV

copolymerised with units of formulae I and/or II, and optionally III above. Preferred aromatic polymers have a reduced viscosity of at least 0.3 (as measured at 25°C on a solution of the polymer in dimethyl formamide containing 1 g of polymer in 100 cm^3 of solution).

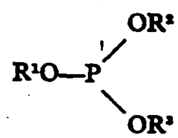
Methods for making such polymers are described, inter alia, in British Patent Specifications 1 016 245; 1 060 546; 1 078 234; 1 109 842; 1 122 192; 1 133 561; 1 153 035; 1 153 528; 1 177 183; 1 234 301; 1 264 900; 1 298 821; Canadian Specification 847 963 and Swiss Specification 491 981.

By the term univalent hydrocarbon or halohydrocarbon radical we mean alkyl, cycloalkyl, haloalkyl, aralkyl, alkaryl, haloalkaryl or aryl radicals. In a simple phosphite ester R^1, R^2 and R^3 may be the same or different but not more than 1, and preferably none, of the radicals R^1, R^2 and R^3 may be hydrogen. The alkyl radical may contain 1 to 25 carbon atoms and may be straight chain or branched. Lower alkyl (1 to 5 carbon atoms) may lead to phosphite esters having too high volatility for a particular end use for the composition and highly branched phosphite esters may themselves be decomposed by for example oxidation at processing temperatures for the composition. Preferably each alkyl residue contains 7 to 12 carbon atoms. The halogen atom in a haloalkyl radical reduces volatility and increases flame resistance of the thermoplastic composition. Tertiary halogen groups are preferably absent because these often have low stability at high temperatures at which the compositions are processed. The halogen atom is preferably chlorine or bromine. The aryl radical may be derived from benzene, biphenyl or a fused ring aromatic hydrocarbon such as for example naphthalene, indene, fluorene, dibenzofuran. The alkaryl or halcalkaryl radical is an aryl radical in which an alkyl radical or haloalkyl radical as hereinbefore defined substitutes one or more aromatic ring positions of the aryl radical; for example methyl phenyl (tolyl), dimethylphenyl (xylyl), and nonylphenyl.

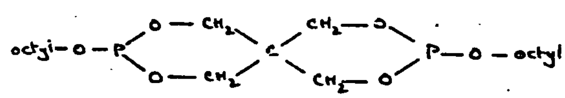
The radicals R^1, R^2 and R^3 may be a univalent radical or R^1, R^2 and/or R^3 taken together may be a multivalent hydrocarbon or halohydrocarbon radical such as a bi-, ter- or quadri-valent radical. By the term multivalent hydrocarbon or halohydrocarbon radical we mean a radical obtained by removal of one or more hydrogen and/or halogen atoms from a univalent hydrocarbon or halohydrocarbon radical as hereinbefore defined. Examples of such multivalent radicals are methylene, propane-1,2,3-triyl, propane-1,3-diyl-2-ylidene. Thus two or three of the radicals R^1, R^2 and R^3 in a single phosphite ester molecule may be a single bi- or ter-valent radical respectively linking at least two oxygen atoms of the phosphite group such as, for example, in the compound



Also the radicals R^1, R^2 and/or R^3 taken together may be a multivalent radical linking two or more phosphite groups of the formula



to provide phosphite esters such as for example



The compositions of the invention may be made by mixing the organic phosphorus compound with the molten polymer by, for example, extrusion or in a sigma-bladed mixer or in a two-roll mill, or by mixing a solution of the phosphorus compound with powdered polymer followed by drying.

The aromatic polysulphone may be blended with other thermoplastic polymeric substances such as, for example, polyesters, polyolefins, polyamides and polyvinyl chloride. The composition may be further mixed with particles of other polymeric materials having special properties, e.g. elastomeric materials and polytetrafluoroethylene. They may contain reinforcing fillers, for example glass, asbestos and carbon fibres, and other materials conferring various desired characteristics, e.g. solid lubricants (e.g. graphite or molybdenum disulphide), abrasives (e.g. carborundum), friction-conferring materials, magnetic materials (e.g. for recording tapes), photosensitisers, and any other materials for which the compositions of the invention make suitable vehicles. The compositions may contain dyes and pigments. The compositions may be fabricated in any desired form, such as fibre, film and mouldings or extruded products of any desired shape.

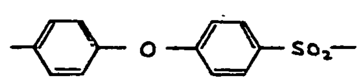
In a modification of the present invention 25 to 75% (preferably 25 to 50%) by weight of the phosphite ester can be replaced by a phosphate ester having the formula $(EO)_3PO$ where E has the same definition as R^1, R^2, R^3 (herein before defined) except that E cannot be hydrogen.

Incorporation of 0.01% to 4% by weight of phosphite ester improves the melt stability of the aromatic polysulphone and its blends by reducing the tendency of the melt viscosity to increase on prolonged heating and provides mouldings having improved colour which is maintained even after prolonged heating of the melt. A preferred level of inclusion of organic phosphorus compound is 0.01 to 1% by weight.

The invention is illustrated by the following Examples.

EXAMPLE 1.

Samples (100 g) of aromatic polysulphone consisting essentially of repeating units of the formula



made in a manner similar to that of Example 3 of British Specification 1 153 035 but having a reduced viscosity of 0.48 as measured at 25°C on a solution in dimethyl

formamide of 1 g of polymer in 100 cm^3 of solution was mixed with a variety of stabilisers in concentration shown in the following table (e.g. 0.2% which is 0.2 g stabiliser per 100 g polymer). Where the stabilisers were solid at 20°C, mixing was effected by dry mixing at 20°C; where stabilisers were liquid at 20°C, the stabilisers were diluted with methanol together with a minimum of acetone to improve miscibility and the polymer stirred into the solution, the resulting mixture being partially dried on a rotary evaporator for 30 minutes at 40°C and finally dried for 20 hours at 150°C. The compositions from both mixing procedures were compression-moulded at 350°C for 5 minutes.

The mouldings and mixtures were evaluated for colour and stability as follows:—

1. Melt viscosity. The melt viscosity was studied using a ram extruder having a barrel temperature of 400°C and the time taken from feeding the mixture to the barrel to exhibit an increase in melt viscosity of 0.1 poise (a) and 0.2 poise (b) recorded; the longer the time, the better the melt stability.
2. Extrudate 50% bubbles. This test provides the time taken at 400°C for half the volume of the extrudate of the extruder used in melt-viscosity determination (1 above) to be voids or bubbles. The test provides a measure of heat stability of the composition and the lower the time, the poorer the heat stability of the composition.
3. Colour factor. The yellowness Index was determined using a General Electric-Hardy recording spectrometer according to the method of ASTM D1925. The % transmission was derived from the Yellowness Index by integration over the visible spectrum.

Results of physical testing of the compositions of Table 1A are presented in Table 1B.

TABLE 1A

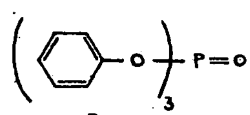
No.	Stabiliser Name	%	Formula
A	None	–	–
B	Triphenyl phosphate	0.1	I
C	Triphenyl phosphate	0.2	I
D	Triphenyl phosphite	0.2	II
E	Tri(nonylphenyl)phosphite (nonylated triphenylphosphite) 1*	0.2	
F	Tri(nonylphenyl)phosphite 2*	0.2	III
G	Tridecyl phosphate 3*	0.2	
H	Di(isodecyl)phosphite 4*	0.2	IV
I	Diphenyl phosphite	0.2	
J	Tri(methyl cyclohexyl)phosphite	0.2	V
K	Tri(chloroethyl)phosphite	0.2	VI
L	Distearyl pentaerythritol diphosphite 5*	0.2	VII
M	Diisooctyl pentaerythritol diphosphite	0.2	
N	Tri(dipropylene glycol)phosphite 6*	0.2	VIII

1* "Polygard" Rubber Regenerating Co. Manchester.
2* "Phosclere" 315 Interstab Limited, Kirkby, Liverpool.
3* "Phosclere" 310 Interstab Limited, Kirkby, Liverpool.
4* "Phosclere" 210 Interstab Limited, Kirkby, Liverpool.
5* Weston 618 Weston Chemical Inc. N.Jersey, U.S.A.
6* Weston Chemical Inc. N.Jersey, U.S.A.

["Polygard" and "Phosclere" are Registered Trade Marks]

TABLE 1B

Composition	Melt viscosity (400°C) Time (minutes) to increase by (a) 0.1 poise	(b) 0.2 poise	Extrudate 50% bubbles (minutes)	Colour Factors Yellow Index	% trans-mission
A	16	24	5	59.3	42.7
B	27	40	5	60.7	48.2
C	31	47	10	62.4	47.9
D	43	53	15	46.1	51.4
E	35	48	20	48.3	55.6
F	35	47	20	42.0	60.4
G	38	50	30	36.6	62.2
H	38	48	20	43.8	59.1
I	36	49	15	38.1	60.6
J	36	48	25	40.3	62.9
K	35	46	25	38.6	63.3
L	30	41	15	35.9	65.1
M	36	45	20	37.1	61.1
N	26	36	20	43.0	60.5
Required Value	high	high	high	low	high



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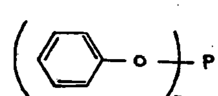

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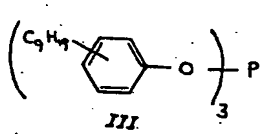

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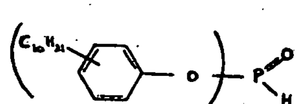

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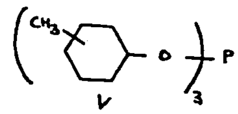
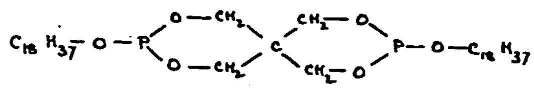


V

$(Cl\,CH_2CH_2O)_3P$

VI



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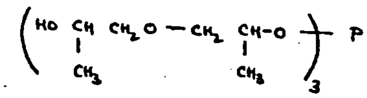


VIII

From the table 1B, it is seen that the comparative compositions, B, C and N, are unsatisfactory in certain respects. Thus triphenyl phosphate, (compositions B and C) offers no improvement in yellow index while tri(dipropylene glycol) phosphite is not very effective in retarding viscosity increase.

EXAMPLE 2.

The procedure of Example 1 was repeated except that the polymer and stabiliser were mixed on a "Henschel" mixer at 60°C followed by extrusion at 330°C. Melt stability was determined using granulated extrudate. Colour Factor was measured on plaques injection moulded at 350°C. The results of this testing is presented in Table 2.

TABLE 2

Additive	% by weight	Melt viscosity (400°C) Time (minutes) to increase by (a) 0.1 poise	(b) 0.2 poise	Extrudate 50% bubbles (minutes)	Colour Factors Yellow Index	% trans-mission
None	—	29	46	50	62.3	44.6
Triphenyl phosphate ┼	0.1	25	37	30	56.2	50.0
Triphenyl phosphate ┼	0.2	39	52	20	63.4	45.3
Triphenyl phosphite	0.1	46	67	60	51.9	53.7
Triphenyl phosphite	0.2	52	72	60	45.5	56.2
Tri(nonylphenyl)-phosphite 1*	0.1	49	70	50	51.1	53.8
Tri(nonylphenyl)-phosphite 1*	0.2	55	74	60	46.8	56.9
Trilauryl phosphite 2*	0.1	52	69	20	47.6	56.4
Trilauryl phosphite 2*	0.2	43	48	25	42.7	59.8

1* "Phosclere" 315 } Interstab, Kirkby, Liverpool.
2* "Phosclere" 312 }

┼ comparative

EXAMPLE 3.

The procedure of Example 2 was repeated to demonstrate that phosphites mixtures and phosphite/phosphate mixtures conferred stability on aromatic polysulphones. The results and composition details are presented in Table 3A and B.

TABLE 3A

Composition	Additive	% by weight
F	None	—
Q	Trilauryl phosphite 1*	0.05
	Triphenyl phosphite	0.05
R	Trilauryl phosphite 1*	0.05
	Triphenyl phosphate	0.05
S	Tri(nonylphenyl)phosphite 2*	0.05
	Triphenyl phosphate	0.05
T	Trilauryl phosphite 1*	0.05
	Tri(nonylphenyl)phosphite 2*	0.05

1* "Phosclere" 312

2* "Phosclere" 315

TABLE 3B

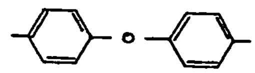
Composition	Melt viscosity (400° C) Time (minutes) to increase by		Extrudate 50% bubbles (minutes)	Colour Factors	
	(a) 0.1 poise	(b) 0.2 poise		Yellow Index	% trans-mission
P	29	46	50	62.3	44.6
Q	43	61	45	49.0	55.2
R	43	59	40	50.4	54.7
S	43	64	60	47.5	56.2
T	45	61	40	50.2	55.4

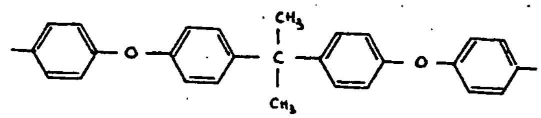
WHAT WE CLAIM IS:—

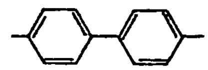
1. A thermoplastic polymer composition having improved thermal stability comprising at least one aromatic polysulphone consisting of repeating units having the structure

$$—Ar—SO_2—$$

wherein Ar which may vary from unit to unit in the polymer chain, is a bivalent aromatic radical selected from







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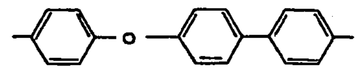
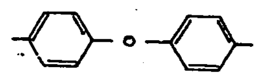
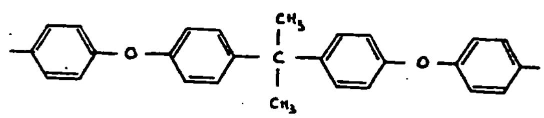


at least some of said Ar radicals being



and/or



and at least one phosphite ester, the amount of said phosphite ester being 0.01 to 4% by weight, based on the combined weights of the phosphite ester and polysulphone, said phosphite having the formula

$$R^1O{-}P\begin{matrix}\diagup OR^2\\ \diagdown OR^3\end{matrix}$$

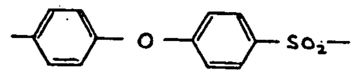
in which R^1, R^2 and R^3 are selected from hydrogen and univalent hydrocarbon or halohydrocarbon radicals, as hereinbefore defined, provided that not more than one of R^1, R^2 and R^3 is hydrogen, or R^1, R^2 and/or R^3 taken together form a multivalent hydrocarbon or halohydrocarbon radical, as hereinbefore defined, linking a) two or more phosphite groups of the formula

$$R^1O{-}P\begin{matrix}\diagup OR^2\\ \diagdown OR^3\end{matrix}$$

or b) at least two oxygen atoms of the same phosphite group.

2. A composition according to Claim 1 wherein the amount of phosphite ester is 0.01 to 1% by weight, based on the combined weights of the phosphite ester and polysulphone.

3. A composition according to Claim 1 or Claim 2 in which the aromatic polysulphone comprises repeating units of the formula



4. A composition according to any one of Claims 1 to 3 in which one phosphite ester is present in the composition.

5. A composition according to any one of Claims 1 to 4 in which none of the radicals R^1, R^2, R^3 in the phosphite ester is hydrogen.

6. A composition according to Claim 5 in which the phosphite ester is tri(nonylphenyl) phosphite.

7. A composition according to Claim 5 in which the phosphite ester is trilauryl phosphite.

8. A composition according to Claim 5 in which the phosphite ester is triphenyl phosphite.

9. A modification of the composition claimed in any one of Claims 1 to 8 in which 25% to 75% by weight of the phosphite ester is replaced by a phosphate ester having the formula $(EO)_3PO$ where E has the same definition as R^1, R^2, R^3 save that E cannot be hydrogen.

10. A modified composition according to Claim 9 in which the phosphate ester is triphenyl phosphate.

11. A modified composition according to either Claim 9 or 10 in which the phosphite ester is tri(nonylphenyl) phosphite.

12. A composition according to Claim 1 substantially as hereinbefore described and illustrated with reference to any one of the Examples.

13. A modified composition according to Claim 9 substantially as hereinbefore described and illustrated with reference to Example 3.

14. A composition according to any one of Claims 1 to 8 and 12 or a modified composition according to any one of Claims 9 to 11 and 13 in the form of a thermoformed article.

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